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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICANT(S): Eugene A. Fitzgerald  
CONFIRMATION NO.: 5381  
SERIAL NO.: 10/022,689 GROUP NO.: 2813  
FILING DATE: December 17, 2001 EXAMINER: Laura M. Schillinger  
TITLE: CONTROLLING THREADING DISLOCATION DENSITIES IN  
Ge ON Si USING GRADED GeSi LAYERS AND  
PLANARIZATION

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Commissioner for Patents  
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Alexandria, VA 22313-1450

**COMMENTS ACCOMPANYING REQUEST  
FOR PRE-APPEAL BRIEF CONFERENCE**

This paper is submitted along with a Pre-Appeal Brief Request for Review in accordance with the Official Gazette Notice dated July 12, 2005, and a Notice of Appeal in response to the Office Action mailed by the U.S. Patent and Trademark Office on August 24, 2005. A fee for filing the Notice of Appeal is submitted herewith. Any other fees necessary for the entry and consideration of this paper should be charged to Deposit Account No. 07-1700.

Applicant's **Remarks** begin on page 2 of this paper.

## REMARKS

In maintaining her rejection, the Examiner argues that a silicon nitride layer that is “silicon rich” qualifies as a “semiconductor” layer. The Examiner offers nothing in support of this contention, and for good reason: it is incorrect as a matter of semiconductor physics, and particularly so in light of the plain teaching of the reference she cites.

As is well known, a semiconductor is a “solid crystalline material whose electrical conductivity is intermediate between that of a metal and an insulator.”<sup>1</sup> Silicon nitride, by contrast, is *not* crystalline and is an *insulator* rather than a semiconductor — whether or not it is “silicon rich.” This is apparent not only from recognized texts, but from the very patent (Thakur et al.) cited by the Examiner.

Submitted herewith is an excerpt from *Silicon Processing for the VLSI Era*,<sup>2</sup> which states that “[s]ilicon nitride films are amorphous insulating materials[.]”<sup>3</sup> In other words, they are (non-crystalline) insulators rather than (crystalline) semiconductors. The discussion in this reference expressly refers to *silicon-rich nitrides*<sup>4</sup> as merely having a higher refractive index, not as different in insulating character from other silicon nitrides.

Indeed, the Thakur et al. patent itself, on which the Examiner relies, is inconsistent with a characterization of silicon nitride as a semiconductor:

- Thakur et al. characterize their silicon nitride layers (even the silicon-rich ones) as oxidation masks; see col. 3, lines 13-14. If the silicon nitride were actually a semiconductor like silicon, it would oxidize in an oxidizing ambient; indeed, Thakur

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<sup>1</sup> *Dictionary of Scientific and Technical Terms*, McGraw-Hill (1974).

<sup>2</sup> Lattice Press (1986).

<sup>3</sup> *Id.* at 191.

<sup>4</sup> *Id.* at 193.

et al. implicitly contrast a silicon nitride mask with “a semiconductor such as silicon” (col. 3, lines 12-14).

- Thakur et al. specify the index of refraction for silicon-rich nitride as “about 3.0” (see col. 3, line 44). The index of refraction of silicon is 3.42, i.e., substantially different from that of even silicon-rich nitride, as noted above in connection with the *Silicon Processing* reference. This is one more indication that the silicon-rich nitride contemplated by Thakur et al. is not similar enough to silicon be considered a semiconductor.
- The etchants Thakur et al. use to remove the silicon nitride, namely, HF or hot phosphoric acid (see col. 4, lines 51-52), will not etch silicon. In fact, Thakur et al. must provide an alternative method to etch silicon (see col. 4, lines 26-30), namely, dry etching with a fluorine chemistry or  $\text{CF}_4/\text{O}_2$  plasmas.
- Fundamentally, Thakur et al. utilize silicon-rich nitride to exert compressive stress on underlying silicon (see col. 3, lines 61-63). This is simply inconsistent with the material being sufficiently silicon-like to qualify as a semiconductor, since if it were, it could not fulfill the intended function of exerting stress on silicon.

**CONCLUSION**

We respectfully submit that, as set forth in the foregoing remarks, there are clear errors in the Examiner's rejections.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Steven J. Frank', is written over a horizontal line.

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# SILICON PROCESSING FOR THE VLSI ERA

VOLUME 1:

PROCESS TECHNOLOGY

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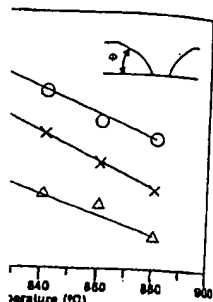
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source gases for B and P compete with one another for inclusion into the final deposited film. This makes for a complex relation of reactant gas composition to eventual film doping<sup>36</sup>.

The chemical composition of BPSG (and PSG), can be determined by several techniques, including the following: a) *wet chemical colorimetry*, which is the most accurate, analyzes the dissolved BPSG film; b) *x-ray photoelectron spectroscopy* (see Chap. 17), which is useful for determining the phosphorus content of the film; c) *Fourier transform infrared spectroscopy* (see Chaps. 1 and 5) which can measure boron levels quite accurately, but phosphorus levels less well accurately (due to the presence of a partially obscured phosphorus-oxygen absorption band); and d) *film etch rates in buffered HF*. Since the etch rate of BPSG in buffered HF depends on the concentration of both B and P in the film, a determination of the etch rate can provide a rapid, qualitative comparison of the composition between BPSG samples.

### PROPERTIES AND CHEMICAL VAPOR DEPOSITION OF SILICON NITRIDE

Silicon nitride films are amorphous insulating materials that find three main applications in VLSI fabrication: 1) as final passivation and mechanical protective layers for integrated circuits, especially for parts encapsulated in plastic packages; 2) as a mask for the selective oxidation of silicon; and 3) as a gate dielectric material in MNOS devices. Silicon nitride also has a high dielectric constant (6.9 vs  $\sim 4.2$  for CVD  $\text{SiO}_2$ ), making it less attractive for interlevel insulation, because of the resultant higher capacitance between conductor layers.

Silicon nitride is highly suitable as a *passivation layer* because of its following properties: a) it behaves as a nearly impervious barrier to diffusion (in particular, moisture and sodium find it very difficult to diffuse through the nitride film); b) it can be prepared by PECVD to have a low compressive stress, which allows it to be subjected to severe environmental stress with less likelihood of delamination or cracking; c) its coverage of underlying metal is conformal; and d) it is deposited with acceptably low pinhole densities.

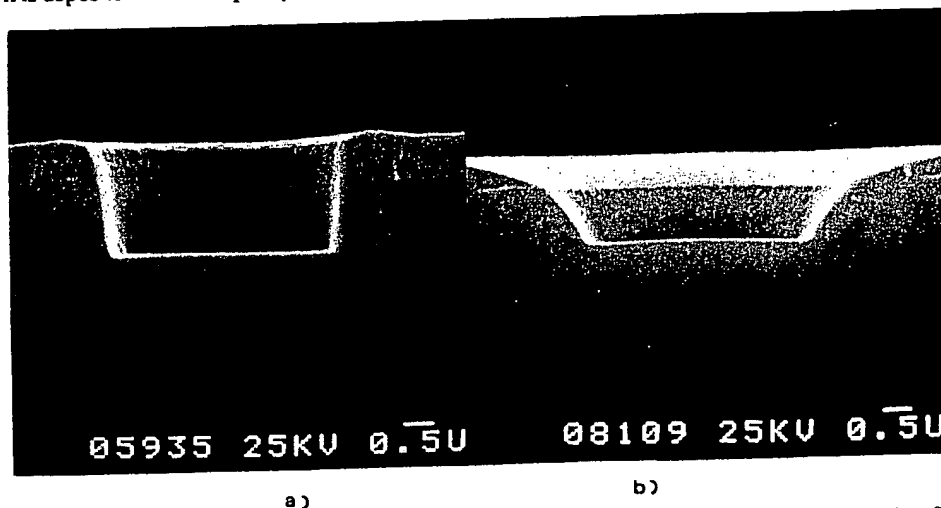


Fig. 24 (a) SEM of dry-etched contact window before reflow. (b) Reflowed BPSG film with 4 wt% P and 4 wt% B. Reflow was  $930^\circ\text{C}$  in  $\text{N}_2$  for 25 min<sup>37</sup>. Courtesy of Applied Materials, Inc.

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Silicon nitride is useful as a *masking layer for selective oxidation*<sup>44</sup>, since oxygen also finds it difficult to penetrate silicon nitride. That is, silicon nitride is deposited directly on a silicon substrate (actually onto a thin, thermal stress-relief  $\text{SiO}_2$  layer, called a *pad oxide*) and patterned. The wafer is then subjected to an oxidation step. The silicon nitride itself oxidizes very slowly, but is not penetrated by the oxygen. As a result it protects the underlying Si from oxidizing, while allowing a thermal  $\text{SiO}_2$  layer to grow on regions of exposed Si. For example, at 1000°C in steam for 10 hours, only a few hundred Å of silicon nitride is converted to  $\text{SiO}_2$ , while more than 1  $\mu\text{m}$  of  $\text{SiO}_2$  can be grown on the exposed silicon. The silicon nitride is removed after the oxidation step.

As shown in Table 3, two techniques are used for depositing silicon nitride. When used as a mask for selective oxidation or as a gate dielectric material in MNOS structures, silicon nitride is generally deposited by high-temperature (700-800°C) LPCVD techniques, for reasons of film uniformity and lower processing cost<sup>8,31</sup>. When used as a passivation layer, the deposition process must be compatible with such low-melting-point metals as aluminum. Thus silicon nitride must be deposited by a low temperature process (300-400°C). For such applications PECVD is the deposition method of choice, as it can deposit nitride films at 200-400°C<sup>32,43,44</sup>. PECVD silicon nitride, however, tends to be nonstoichiometric, and

## CHEMICAL VAPO

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Table 3. Properties of PECVD Silicon Nitride and High Temperature CVD Nitride

Property	HT-CVD—NP 900°C	PE-CVD—LP 300°C
Composition	$\text{Si}_3\text{N}_4$	$\text{Si}_x\text{N}_y\text{H}_z$
Si/N ratio	0.75	0.8–1.0
Density	2.8–3.1 g/cm <sup>3</sup>	2.5–2.8 g/cm <sup>3</sup>
Refractive index	2.0–2.1	2.0–2.1
Dielectric constant	6–7	6–9
Dielectric strength	$1 \times 10^7$ V/cm	$6 \times 10^6$ V/cm
Bulk resistivity	$10^{12}$ – $10^{17}$ ohms/cm	$10^{13}$ ohms/cm
Surface resistivity	$> 10^{13}$ ohms/square	$1 \times 10^{13}$ ohms/square
Stress at 23°C on Si	$1.2$ – $1.8 \times 10^{10}$ dyn/cm <sup>2</sup> (tensile)	$1$ – $8 \times 10^9$ dyn/cm <sup>2</sup> (compressive)
Thermal expansion	$4 \times 10^{-6}/^\circ\text{C}$	$>4$ – $7 \times 10^{-6}/^\circ\text{C}$
Color, transmitted	None	Yellow
Step coverage	Fair	Conformal
H <sub>2</sub> O permeability	Zero	Low–none
Thermal stability	Excellent	Variable $> 400^\circ\text{C}$
Solution etch rate		
HFB 20–25°C	10–15 Å/min	200–300 Å/min
49% HF 23°C	80 Å/min	1500–3000 Å/min
85% H <sub>3</sub> PO <sub>4</sub> 155°C	15 Å/min	100–200 Å/min
85% H <sub>3</sub> PO <sub>4</sub> 180°C	120 Å/min	600–1000 Å/min
Plasma etch rate		
70% CF <sub>4</sub> /30% O <sub>2</sub> , 150 W, 100°C	200 Å/min	500 Å/min
Na <sup>+</sup> penetration	$< 100$ Å	$< 100$ Å
Na <sup>+</sup> retained in top 100 Å	$> 99\%$	$> 99\%$
IR absorption		
Si–N max	$\sim 870$ cm <sup>-1</sup>	$\sim 830$ cm <sup>-1</sup>
Si–H minor	—	2180 cm <sup>-1</sup>

Fig. 25 Effect of Solid State T



<sup>14</sup>, since oxygen also deposited directly on a lled a *pad oxide*) and nitride itself oxidizes ne underlying Si from sed Si. For example, is converted to SiO<sub>2</sub>. The silicon nitride is

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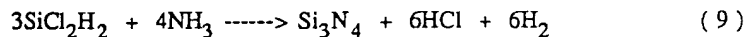
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contains substantial quantities of atomic H (10-30 at%). For this reason it is sometimes chemically represented as Si<sub>x</sub>N<sub>y</sub>H<sub>z</sub>. Comparison of the refractive index of CVD silicon nitride with that of thermal silicon nitride gives a quick estimate of the stoichiometry of the CVD film. Higher refractive indices indicate silicon rich films. Table 3 compares the properties of LPCVD and PECVD silicon nitride films.

*LPCVD silicon nitride* is formed by reacting dichlorosilane (SiCl<sub>2</sub>H<sub>2</sub>) and ammonia (NH<sub>3</sub>) at temperatures between 700-800°C according to the overall reaction:



Silicon nitride depositions by LPCVD are controlled by a large number of deposition parameters including, temperature, total pressure, reactant ratios, and temperature gradients in the reactor. The deposition rate increases with increasing total pressure, or SiCl<sub>2</sub>H<sub>2</sub> partial pressure, but decreases as the [NH<sub>3</sub>] : [SiCl<sub>2</sub>H<sub>2</sub>] ratio gets larger. A temperature ramp, as discussed in the section on hot-wall tube LPCVD reactors, is required for obtaining uniform depositions. In general, LPCVD silicon nitride films have a high density (2.9-3.1 g/cm<sup>3</sup>), a dielectric constant of 6, and are more stoichiometric than PECVD silicon nitride films. Their etch rate in buffered HF is very slow (less than 10 Å/min), and their hydrogen content (up to 8 at%) is less than in PECVD films. In addition, they exhibit excellent step coverage and relatively low particulate contamination. Such films, however, have tensile stresses of ~1x10<sup>10</sup> dynes/cm<sup>2</sup>, which is about an order of magnitude higher than that of TEOS-deposited SiO<sub>2</sub>. This may cause LPCVD silicon nitride films greater than ~2000 Å to crack. Sufficient NH<sub>3</sub> is also needed to insure that all of the SiH<sub>4</sub> is consumed. If insufficient NH<sub>3</sub> is available, the films become silicon rich. As a result, depositions are usually carried out with significant excess flow of NH<sub>3</sub>. It should also be mentioned that, as described in Chap. 7, an anneal in hydrogen is often performed on MOS circuits to reduce the interface trapped charge density, Q<sub>it</sub>, after the final Al layer is deposited and patterned. Since silicon nitride is such an impervious diffusion barrier, this anneal must be performed on wafers prior to depositing a silicon nitride passivation layer.

*Silicon nitride deposition by PECVD* was described by Sterling and Swann in 1965. The

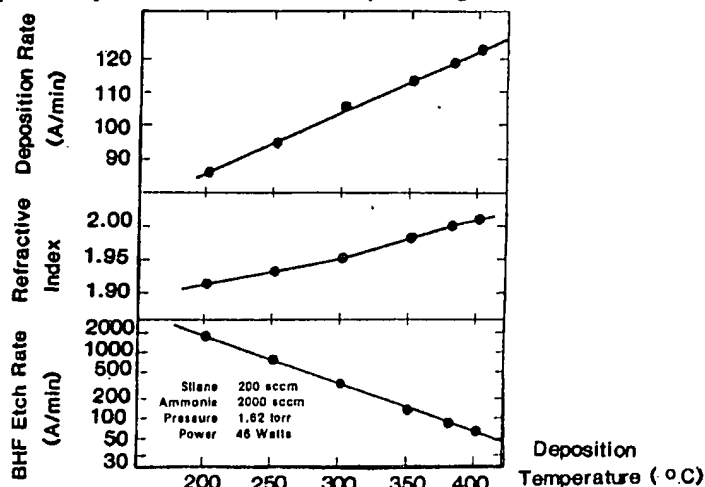


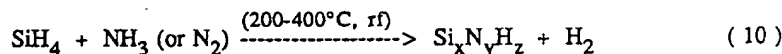
Fig. 25 Effect of deposition temperature on PECVD nitride parameters. Reprinted by permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet<sup>12</sup>.

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Table 4. CVD DEPOSITION REACTIONS

PRODUCT	REACTANTS	METHOD	TEMP (°C)	COMMENTS
Polysilicon	SiH <sub>4</sub>	LPCVD	580-650	may be <i>in situ</i> doped
Silicon Nitride	SiH <sub>4</sub> + NH <sub>3</sub>	LPCVD	700-900	
	SiCl <sub>2</sub> H <sub>2</sub> + NH <sub>3</sub>	LPCVD	650-750	
	SiH <sub>4</sub> + NH <sub>3</sub>	PECVD	200-350	
	SiH <sub>4</sub> + N <sub>2</sub>	PECVD	200-350	
SiO <sub>2</sub>	SiH <sub>4</sub> + O <sub>2</sub>	APCVD	300-500	poor step coverage
	SiH <sub>4</sub> + O <sub>2</sub>	PECVD	200-350	good step coverage
	SiH <sub>4</sub> + N <sub>2</sub> O	PECVD	200-350	
	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> [TEOS]	LPCVD	650-750	liquid source, conformal
	SiCl <sub>2</sub> H <sub>2</sub> + N <sub>2</sub> O	LPCVD	850-900	conformal
Doped SiO <sub>2</sub>	SiH <sub>4</sub> + O <sub>2</sub> + PH <sub>3</sub>	APCVD	300-500	PSG
	SiH <sub>4</sub> + O <sub>2</sub> + PH <sub>3</sub>	PECVD	300-500	PSG
	SiH <sub>4</sub> + O <sub>2</sub> + PH <sub>3</sub> + B <sub>2</sub> H <sub>6</sub>	APCVD	300-500	BPSG, low temperature flow
	SiH <sub>4</sub> + O <sub>2</sub> + PH <sub>3</sub> + B <sub>2</sub> H <sub>6</sub>	PECVD	300-500	BPSG, low temperature flow

overall deposition reaction is written as:



where silane and ammonia or nitrogen are reacted in a plasma at 200-400°C. The use of a high (100-1000:1) N<sub>2</sub>: SiH<sub>4</sub> ratio is required to prevent silicon rich film formation (since the N<sub>2</sub> dissociation rate is much lower than that of silane). On the other hand, NH<sub>3</sub> dissociates much more readily, and thus lower NH<sub>3</sub>: SiH<sub>4</sub> ratios can be used (e.g. 5-20:1).

The deposition rate depends strongly on rf power, gas flow, chamber pressure and frequency (Fig. 25). If a PECVD deposition process is to be developed, it would be useful to approach the problem with a statistically-based set of experiments as discussed in Chap. 18. A case study of such a process development effort is found in Ref. 44. The stress in PECVD silicon nitride films can also be changed by altering a variety of deposition conditions.

Infrared spectroscopy shows that an appreciable amount of hydrogen in the form of Si-H and N-H is found in PECVD silicon nitride films. The total amount of hydrogen can reach 18-22 at% in films deposited from SiH<sub>4</sub>-NH<sub>3</sub> near 300°C. Lower hydrogen content is reportedly found in films from SiH<sub>4</sub>-N<sub>2</sub><sup>12</sup>. The presence of large quantities of hydrogen has been reported to be detrimental to IC devices. For example, significant threshold shifts are observed, and etching characteristics (both wet and dry) of the films are impacted. Another advantage of using N<sub>2</sub> rather than NH<sub>3</sub> is that it yields compressive silicon nitride films over a wider range of deposition conditions. Oxygen in the form of Si-O bonds has also been detected in PECVD silicon nitride films. Oxygen concentration increases as the deposition temperature decreases, and is believed to be due to moisture or oxygen released from the reaction chamber walls. Table 4 is a summary of the CVD reactions for poly-Si, SiO<sub>2</sub>, PSG, BPSG, as well as silicon nitride.

Materials called silicon are called silicon NH<sub>3</sub>. Property resistance<sup>45</sup>. Su deposited oxides. refractive index. for use as low-temperature PECVD silicon planarization scheme

## SIPOS

Silicon rich (SIPOS) can also been reported to as an injector in forming emitter SIPOS is SiO<sub>x</sub>, SiH<sub>4</sub> flow rate emission spectrum

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